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Electrokinetic Properties
of Polymer Colloids
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ELECTROKINETIC PROPERTIES OF POLYMER COLLOIDS

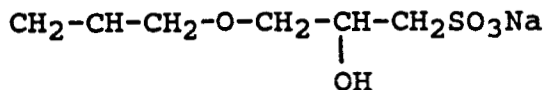
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Objective

The objective of this research effort is to modify the surface of polymer colloids, especially polystyrene latexes, for the purpose of controlling the electrokinetic properties of the resulting colloids. Achievement of this objective requires a knowledge of the electrical double layer charging mechanism, as a function of electrolyte conditions, at the polymer/water interface. The experimental approach is to control the recipe formulation in the emulsion polymerization process so as to systematically vary the strong acid group concentration on the surface of the polymer particles. The electrophoretic mobility of these model particles will then be measured as a function of surface group concentration and as a function of electrolyte concentration and type. An effort will also be made to evaluate the electrophoretic mobility of polystyrene latexes made in space and to compare the results with latexes made on the ground.

Introduction

The stability of a colloidal dispersion depends on the surface characteristics of the particles, and can therefore be controlled by modification of particle surfaces. For the purpose of this investigation polystyrene latexes were prepared with a monomer containing a functional group (sometimes referred to as comonomeric emulsifier or ionogenic comonomer) to alter the colloidal properties of the polymer particles. In the emulsion polymerization of styrene, the sodium salt of a short chain vinyl sulfonate was used as a functional monomer, namely sodium 1-allyloxy 2-hydroxy propyl sulfonate (COPS I). This compound has the following chemical structure.



These polystyrene latexes have been characterized by conductometric titration with sodium hydroxide and hydrochloric acid to determine the surface groups on the latex particles. The electrokinetic properties of the characterized latexes were determined by measuring their electrophoretic mobilities. Electrophoresis measurements are important in colloid stability, ion adsorption and the characterization of particle surfaces. The migration of charged particles relative to the liquid in which they are dispersed under the influence of an external electrical

field is commonly used to measure the zeta potential, which serves as an approximation to the surface potential. An understanding of the nature of the electrical double layer is important in order to interpret electrophoretic mobility data. The potential decays as a function of distance from the surface of the particle, and at some point from the surface of the colloid particle the positive ions must move with respect to the negative ions. The potential at this point, which constitutes the slipping plane, and is located at an unknown distance from the surface, is called the zeta potential and provides the driving force for electrokinetic phenomena.

Results

Batch emulsion polymerization was carried out using the recipe shown in Table I. The materials were poured into a glass bottle, purged with nitrogen (10 min) and tumbled end-over-end in a constant temperature water bath at 70°C for 24 hours.

After polymerization, the aqueous phase of the latex contains impurities such as emulsifier, water soluble polymer and residual initiator

TABLE I
EMULSION POLYMERIZATION RECIPE

INGREDIENTS	
WATER	160.0g
STYRENE	40.0g
NaHCO ₃	0.4g
K ₂ S ₂ O ₈	0.4g
COPS I	Variable

The latexes were cleaned by the serum replacement method. The latexes were washed with distilled deionized water (DDI), followed by a solution of $5 \times 10^{-4} \text{N}$ HCl and again with DDI.

The particle size of the latexes was determined using Transmission Electron Microscopy. Table II shows the particle sizes and polydispersity index of the latexes prepared with COPS I, and Figure 1 shows the electron micrographs of the latex particles prepared with different concentrations of COPS I. The latex particles were polydisperse, and the average particle diameter decreased as the concentration of the functional monomer increased from $2 \times 10^{-2} \text{M}$ to $5 \times 10^{-2} \text{M}$. However, for higher concentration of COPS I, $1 \times 10^{-1} \text{M}$ larger particle sizes were generated.

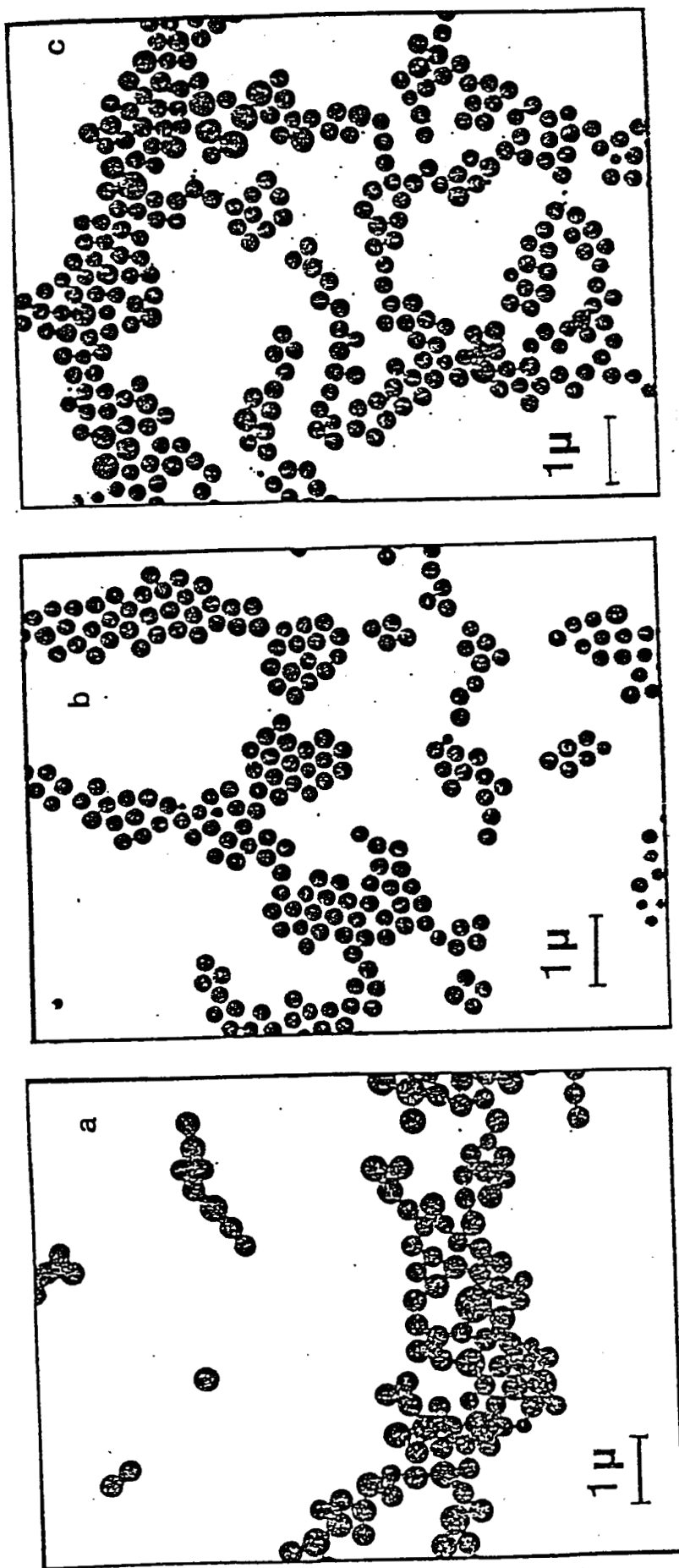


Figure 1: Electron Micrographs of latexes prepared with COPS I: a) $1 \times 10^{-1} \text{M}$; b) $5 \times 10^{-2} \text{M}$; c) $1 \times 10^{-2} \text{M}$

TABLE II

PARTICLE SIZE OF POLYSTYRENE LATEXES PREPARED WITH COPS I

LATEX	[COPS I] (M)	D _n (nm)	D _w (nm)	D _w /D _n
D-1	1X10 ⁻²	642.3	676.7	1.053
D-2	5X10 ⁻²	518.8	526.4	1.015
D-3	1X10 ⁻¹	557.9	586.0	1.050
D-4	2X10 ⁻¹	522.2	532.0	1.060

The surfaces of the latex particles contain sulfate, hydroxyl and carboxyl groups arising from the initiator, as well as sulfonate groups from the functional monomer. The surface characteristics of the latex particles in terms of the type and number of surface groups, were determined by conductometric titration. A weighed amount of purified latex (lg) was diluted to 200 cm³ with distilled water. The latex was stirred with a magnetic stirrer and CO₂ was displaced by passing a stream of nitrogen over the latex surface. The sample was then titrated with standard 0.02N NaOH (forward titration) and 0.02N HCl (back titration). Figures 2 and 3 show the results of conductometric titrations of latexes D-1, D-2, and D-3 in 200 cm³ dispersion, together with a water blank. The conductometric titration curves of all latexes showed the presence of strong acid due to sulfate and sulfonate groups on the particle surfaces, and weak acid (carboxyl) groups. Table III shows the surface charge densities and the area per negative charge on the particles. As the concentration of the functional monomer increased, the surface charge increased, perhaps due to increased incorporation of functional monomer on the particle surface

TABLE III

SURFACE CHARGE DENSITY AND SURFACE AREA PER NEGATIVE CHARGE OF POLYSTYRENE LATEXES PREPARED WITH COPS I

LATEX	[COPS-I] /mol dm ⁻³	STRONG ACID /μC cm ²	WEAK ACID /μC cm ²	SURFACE AREA /Å ² /e ⁻
D-1	1X10 ⁻²	6.18	3.56	259
D-2	5X10 ⁻²	7.78	2.43	206
D-3	1X10 ⁻¹	15.23	2.92	105
D-4	2X10 ⁻¹	18.63	3.15	86

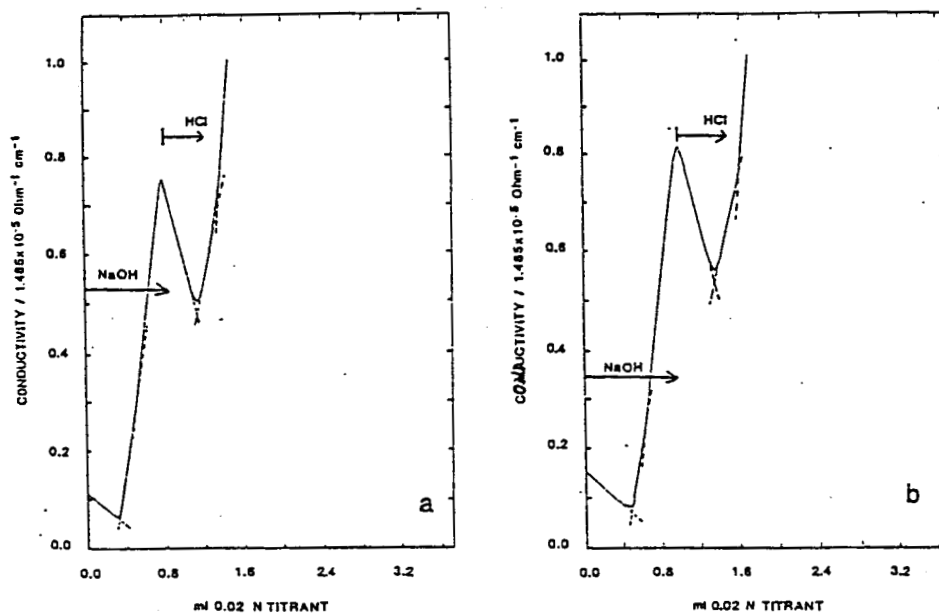


Figure 2: Conductometric Titration: a) Latex D-1 with 0.9980 g solid in 200 cm^3 dispersion, b) Latex D-2 with 0.9310 g solid in 200 cm^2 dispersion, both sparged with nitrogen gas for 5 minutes.

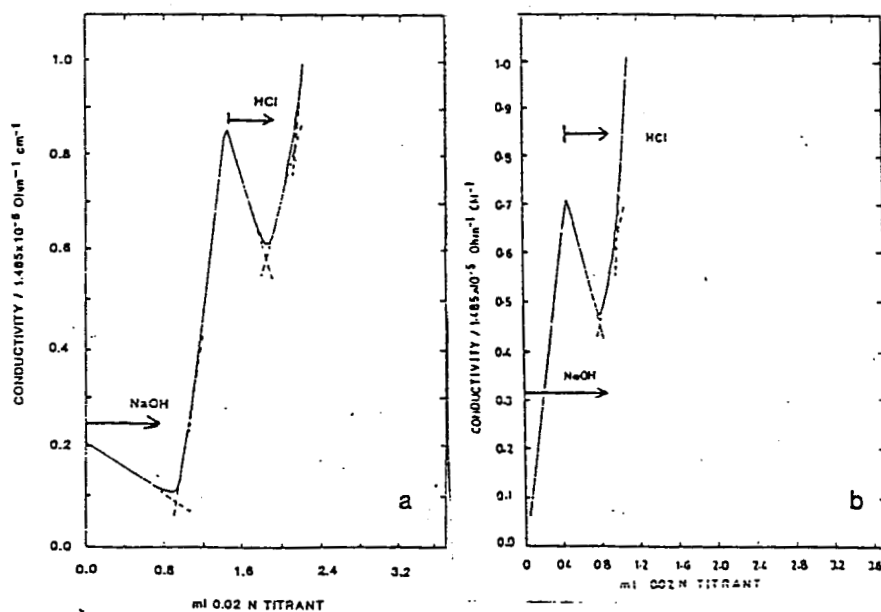


Figure 3: Conductometric Titration: a) Latex D-3 with 0.9977 g solid in 200 cm^3 dispersion, b) Water blank in 200 cm^3 distilled deionized, both sparged with nitrogen gas for 5 minutes.

The particle surfaces were also characterized by electrophoresis measurements in order to exhibit the general characteristic trends of preferential ion adsorption to the latex surfaces. The electrophoretic mobilities of the latexes was measured as a function of pH using the Pen Kem system 3000. A drop of latex was added to a solution whose pH was preadjusted by the addition of NaOH or HCl in conjunction with pH meter. The electrophoretic mobility as a function of pH are shown in Figure 4 for D-1, D-2, and D-3. The results show that all three latexes exhibit the same behavior. At low pH in the range of 2 to 4.6 the mobility increases slightly from -3.57 to -4.17 $\mu\text{cm}/\text{volt sec}$ and then decreases to -2.92 $\mu\text{cm}/\text{volt sec}$ for D-1; for D-2 increases from -3.50 to -4.10 $\mu\text{cm}/\text{volt sec}$ and decreases to -3.07 $\mu\text{cm}/\text{volt sec}$, and for D-3 increases from -3.68 to -4.05 $\mu\text{cm}/\text{volt sec}$ and decreases to -3.29 $\mu\text{cm}/\text{volt sec}$. The initial increase in mobility is attributed to adsorption of anions (Cl^- ions from the added HCl), while the decrease is due to the compression of the electrical double layer. At higher pH, in the range of 8 to 11.5 the latex particles showed an increase in mobility up to -5.86 $\mu\text{cm}/\text{volt sec}$ for D-1, -5.30 $\mu\text{cm}/\text{volt sec}$ for D-2, and -6.26 $\mu\text{cm}/\text{volt sec}$ for D-3, due to adsorption of anions (OH^- ions from the added NaOH). The trend is strong due the presence of sulfate groups. This is followed by a decrease in the surface charge and mobility, due to the effect of the added electrolyte and its effect on compression of the electrical double layer. No appreciable change took place at intermediate pH range since the number of added ions was too small to cause any appreciable changes in mobility.

The particle surfaces were characterized by electrophoresis measurements to observe the general characteristic trends of preferential ion adsorption on the latex surface. The electrophoretic mobility of the latexes was measured as a function of sodium chloride concentration in DDI. The results are shown in Figure 5. It can be seen that each latex shows the same trend. The initial increase in mobility with increasing NaCl concentration to a maximum at about 1×10^{-2} mol dm^{-3} for latexes D-1, D-2 and D-3 and 3×10^{-2} mol dm^{-3} for D-4, was attributed to the adsorption of negative chloride ions from solution on the surface of the latex particle. The decrease in mobility after this maximum is due to double layer compression. Latex D-1, which has the lowest concentration of surface acid groups, shows the greatest tendency toward chloride ion adsorption while latex D-4, which has the highest surface acid concentration, shows less tendency for chloride adsorption.

The electrophoretic mobility of the latexes was also investigated as a function of the concentration of sodium lauryl sulfate in DDI. Figure 6 shows that all latexes exhibit the same behavior. The mobility increases as the concentration of SLS increases to maximum mobility at an SLS concentration of 3×10^{-2} mol dm^{-3} . It can be seen that the anionic surfactant is adsorbed on the surface of each of the latexes. A comparison of latex D-1 and D-4 shows that D-1 has a stronger tendency to

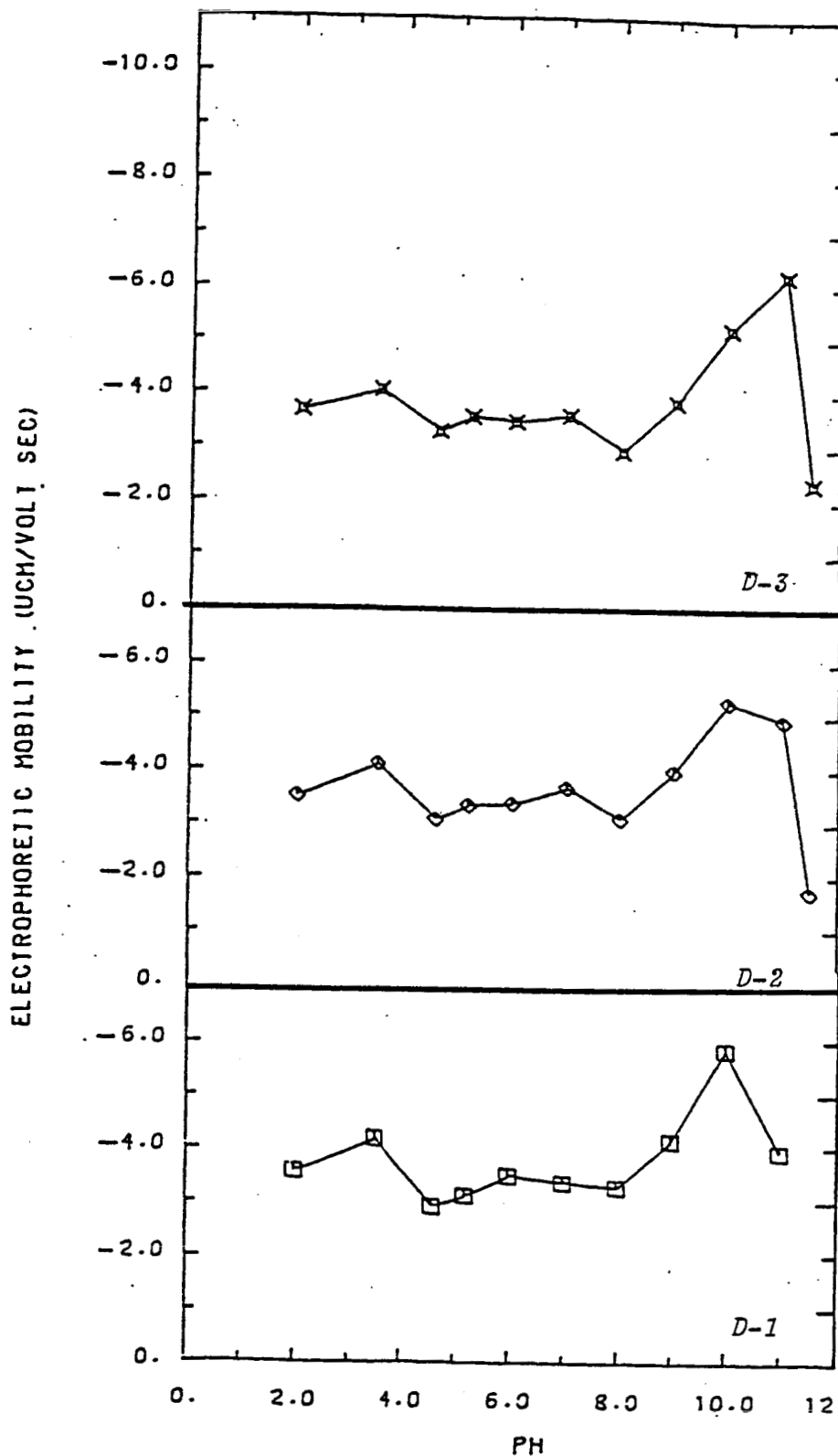


Figure 4: Variation of electrophoretic mobility vs pH for particles of polystyrene, prepared with different concentration of COPS I, in distilled deionized water: D-1 with $1 \times 10^{-2} \text{M}$; D-2 $5 \times 10^{-2} \text{M}$, and D-3 $1 \times 10^{-1} \text{M}$.

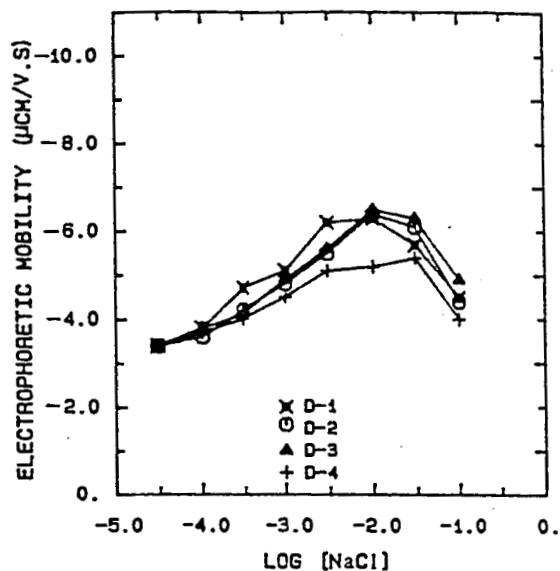


Figure 5: Electrophoretic mobility as a function of log NaCl concentration for particles of polystyrene, prepared with different concentrations of COPS I: D-1 with $1 \times 10^{-2} \text{ mol dm}^{-3}$; D-2 with $5 \times 10^{-2} \text{ mol dm}^{-3}$; D-3 with $1 \times 10^{-1} \text{ mol dm}^{-3}$; and D-4 with $2 \times 10^{-1} \text{ mol dm}^{-3}$.

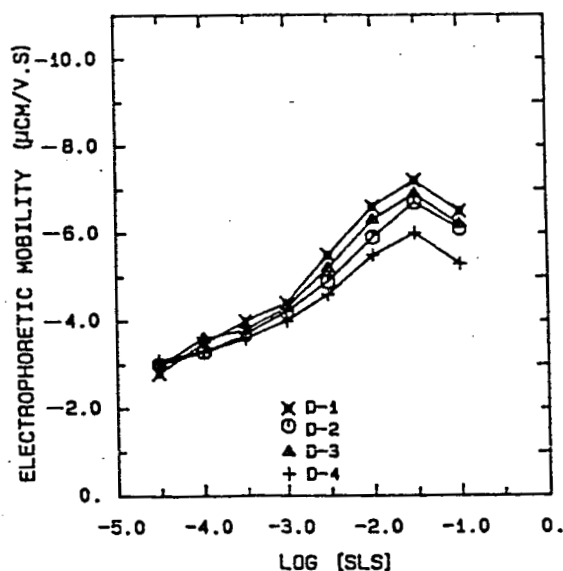


Figure 6: Electrophoretic mobility as a function of log SLS concentration for particles of polystyrene prepared with different concentrations of COPS I: D-1 with $1 \times 10^{-2} \text{ mol dm}^{-3}$, D-2 with $5 \times 10^{-2} \text{ mol dm}^{-3}$, D-3 with $1 \times 10^{-1} \text{ mol dm}^{-3}$; and D-4 with $2 \times 10^{-1} \text{ mol dm}^{-3}$.

adsorb the lauryl sulfate ions than D-4. the controlling mechanism for the generation of surface potential in this case is the hydrophobe-hydrophobe interaction between the bare polystyrene surface and the surfactant.

The electrophoretic mobility of the latexes was measured as a function of the concentration of sodium hydroxide and hydrochloric acid. The results are illustrated in Figures 7 and 8. It can be seen that the latexes show the same trends. The electrophoretic mobility of the particles becomes more negative with increasing NaOH concentration due to the strong adsorption of the hydroxide ion (Figure 3). The decrease in mobility above 1×10^{-2} mol dm⁻³ was attributed to the compression of the electrical double layer. latex D-1 shows a stronger tendency to adsorb the hydroxide ion than D-4, which has the highest surface acid concentration. With HCl, the mobility increases to a maximum at a concentration of 1×10^{-3} mol dm⁻³ for latexes D-2, D-3 and D-4 and 0.02 mol dm⁻³ for D-1, indicating strong adsorption of Cl⁻ ions. The subsequent decrease is attributed to the compression of the electrical double layer.

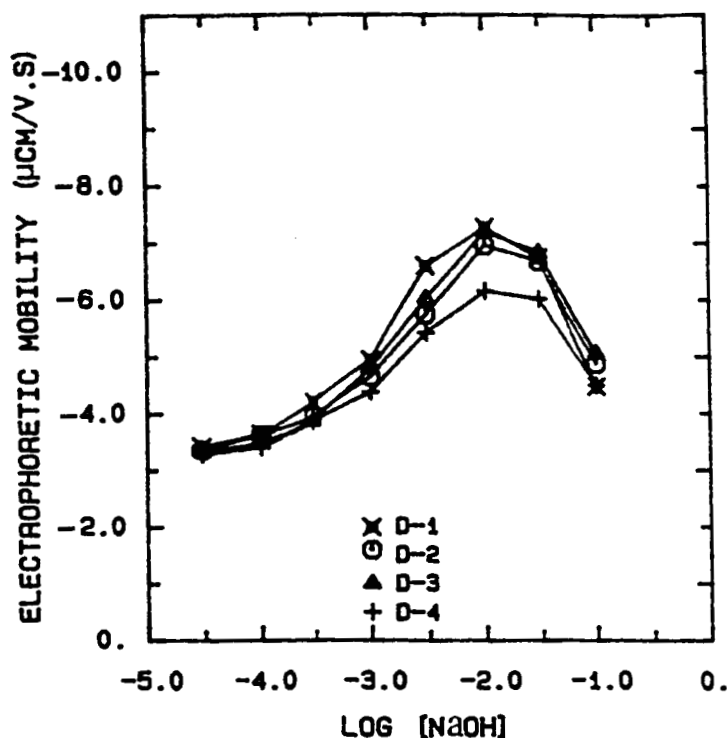


Figure 7: Electrophoretic mobility as a function of log NaOH concentration for particles of polystyrene, prepared with different concentrations of COPS I: D-1 with 1×10^{-2} mol dm⁻³, D-2 with 5×10^{-2} mol dm⁻³, D-3 with 1×10^{-1} mol dm⁻³; and D-4 with 2×10^{-1} mol dm⁻³.

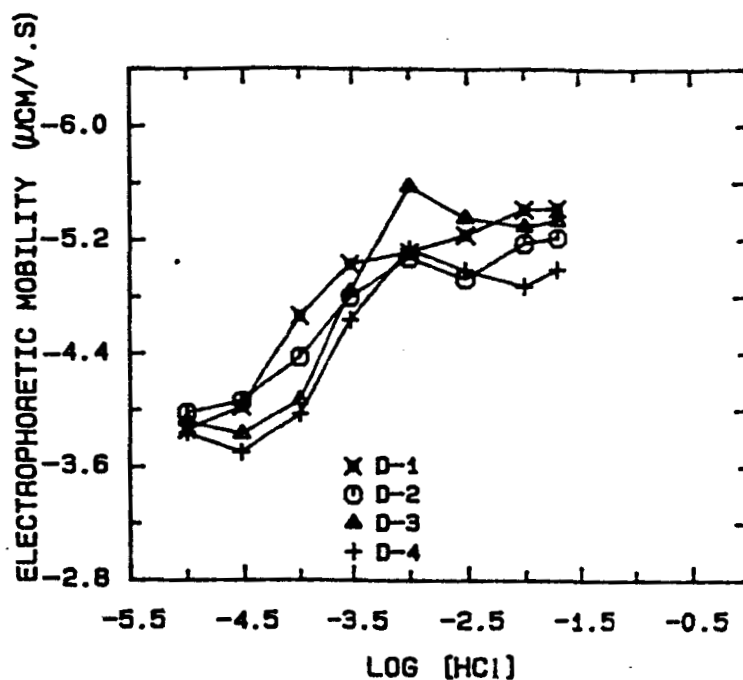


Figure 8: Electrophoretic mobility as a function of log HCl concentration for particles of polystyrene, prepared with different concentrations of COPS I: D-1 with 1×10^{-2} mol dm⁻³, D-2 with 5×10^{-2} mol dm⁻³, D-3 with 1×10^{-1} mol dm⁻³, and D-4 with 2×10^{-1} mol dm⁻³.

The electrophoretic mobilities of latexes D-1 and D-4 were measured in DDI as a function of ethanol concentration. The mobilities were converted to zeta potential using the Smoluchowski equation. The results are given in Figure 9. The results show that the zeta potential of the particles investigated increases with increasing ethanol concentration in a range of 0-30 wt%, followed by an decrease. The increase of zeta potential with ethanol concentration is a indication that the origin of surface charge on these particles is not due entirely to the ionizable surface groups, and that the hydrophobic surface of the latex might be playing a significant role in the origin of the surface charge. The decrease in zeta potential is caused by the lower degree of dissociation of ionizable surface groups due to the lower dielectric constant of ethanol.

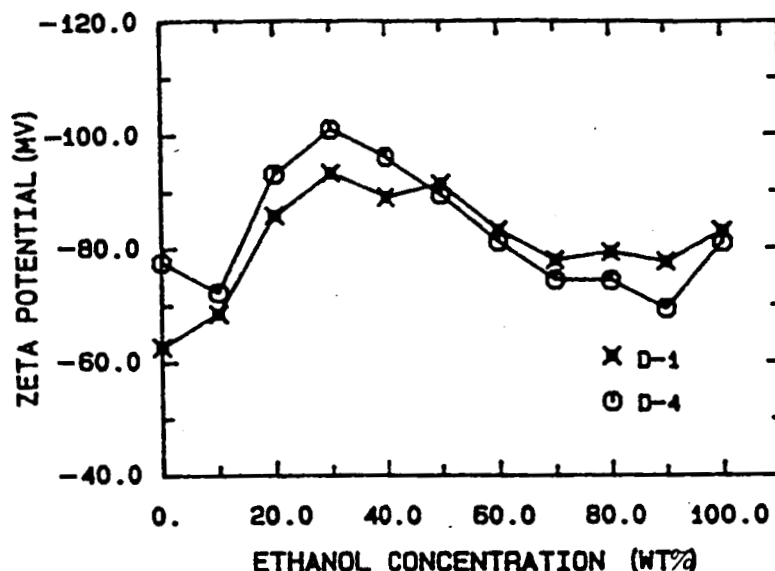


Figure 9: the zeta potential of latexes D-1 and D-4 as a function of the concentration of ethanol.

Figure 10 shows the effect of SLS on the zeta potential of latexes D-1 and D-4 in propanol and water (DDI). The zeta potential of dispersed particles in DDI becomes more negative with the increasing concentration of anionic surfactant (SLS) due to the strong adsorption of the negative LS^- ion. In propanol the zeta potential decreases with the increasing SLS concentration, indicating the preferential adsorption of sodium ion. The preferential adsorption of Na^+ ion in propanol could be due to the lack of solvation of sodium ion in propanol. Latex D-1 shows the greatest tendency toward LS^- and Na^+ ions adsorption.

Figure 11 shows the effect of NaCl on the zeta potential of latexes D-1 and D-4 in ethanol, propanol and DDI. The zeta potential of the latexes in DDI becomes more negative with increasing sodium chloride concentration due to the adsorption of Cl^- ion. In ethanol and propanol the zeta potential decreases with increasing NaCl concentration indicating the preferential adsorption of Na^+ ion. this decrease in charge can also be attributed to a lesser tendency for the LS^- ion to adsorb on the particle surface from a more hydrophobic media than from DDI. Latex D-1 shows the greatest tendency toward Cl^- and Na^+ ions adsorption in propanol, water and ethanol.

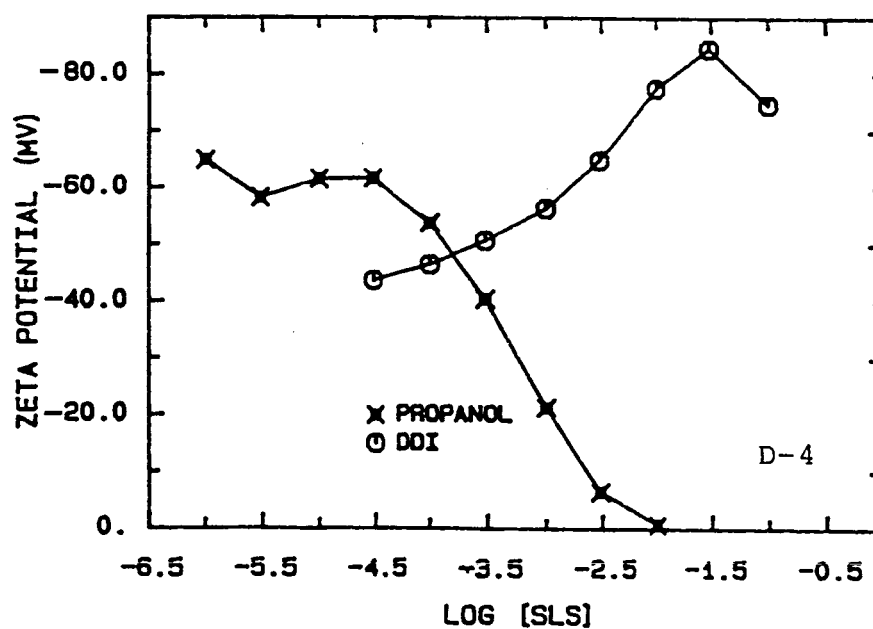
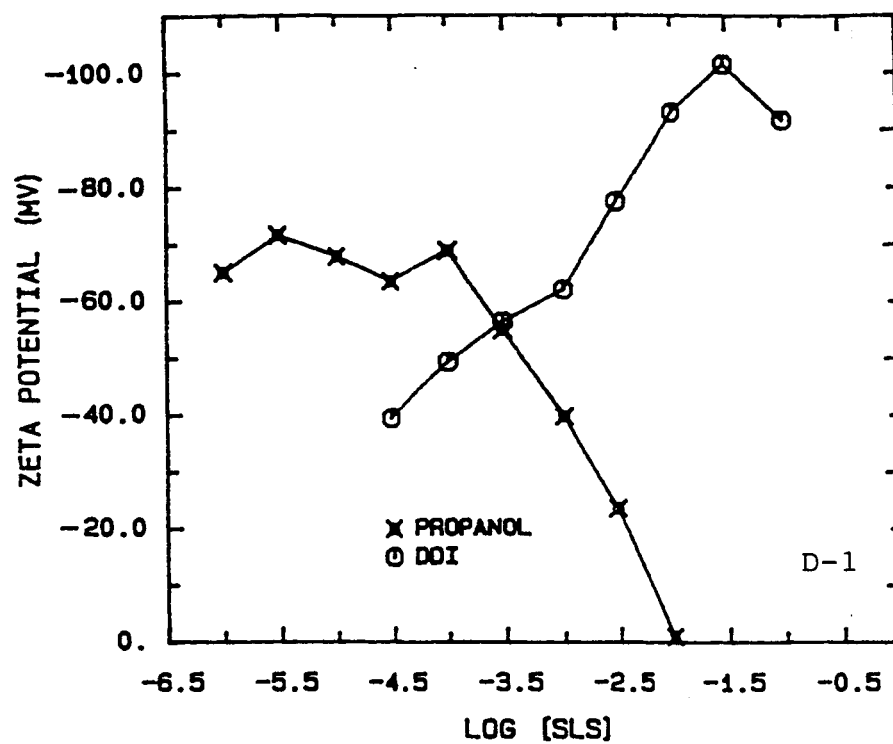


Figure 10: The zeta potential of latexes D-1 and D-4 as a function of log SLS concentration in propanol and DDI.

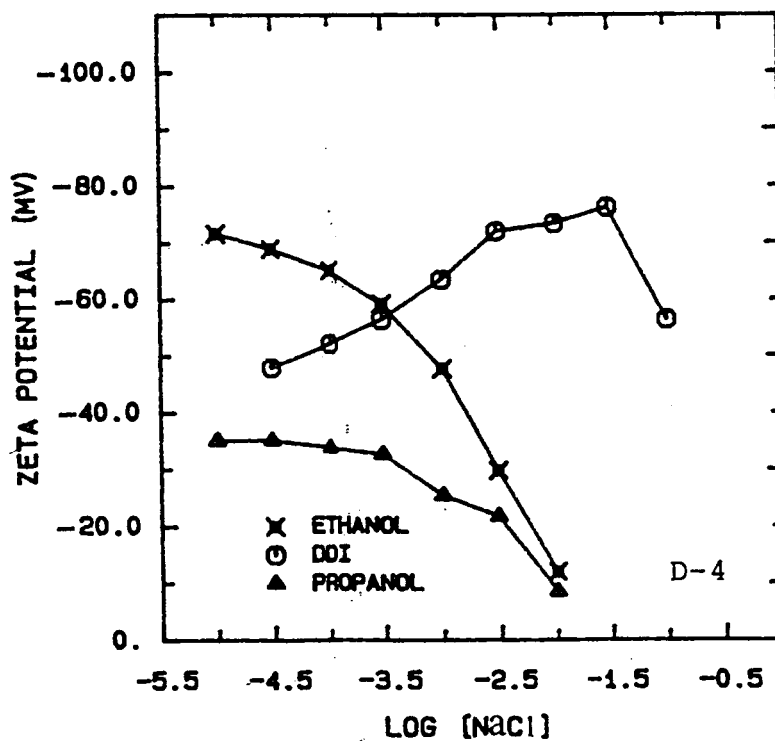
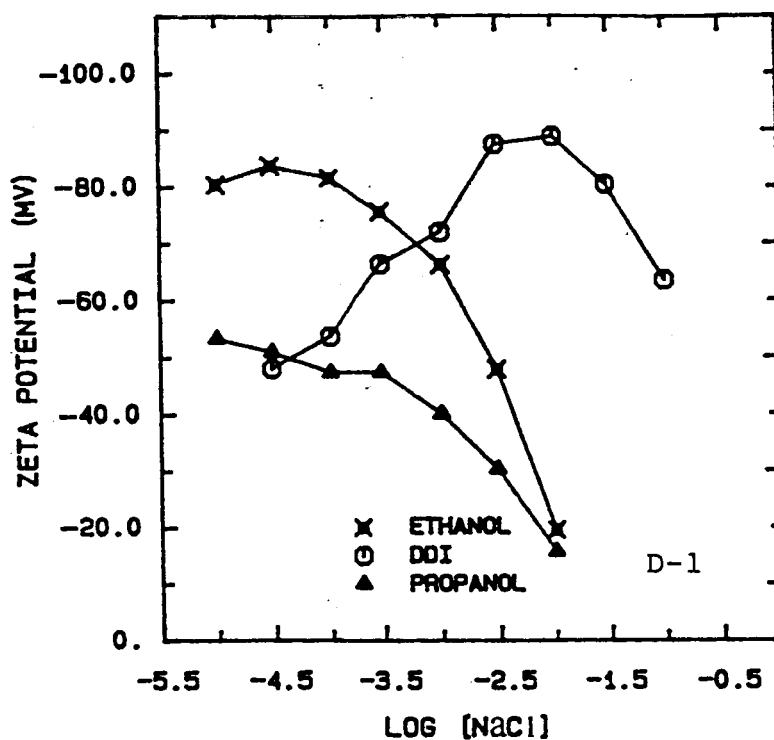


Figure 11: The zeta potential of latexes D-1 and D-4 as a function of log NaCl concentration in propanol, ethanol and DDI.